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(54) **Process for the preparation of quaternary diesters**

Verfahren zur Herstellung von quaternären Diestern

Procédé pour la préparation de diesters quaternaires

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(56) References cited:
EP-A- 0 021 431 **WO-A-93/25648**

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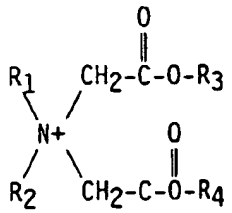
Description

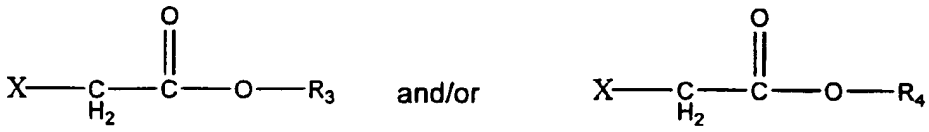
The invention relates to a process for the preparation of quaternary diesters of the formula:



wherein
X^- represents a halogen atom, notably a chlorine atom or a bromine atom, R_1 and R_2 may be the same or different and have the meaning of an alkyl group having 1 to 3 carbon atoms or a hydroxyethyl group, or be linked together to form an alkylene group having 4 to 6 carbon atoms which may be interrupted by an N atom or 0 atom, and R_3 and R_4 may be the same or different and have the meaning of an alkyl group or alkenyl group having 8 to 22 carbon atoms, or be linked together to form an alk(en)ylene group having 8 to 22 carbon atoms, by conversion of a secondary amine of the formula R_1-NH-R_2 with halogen acetate esters of the formulae X-CH_2-C(O)-O-R_3 and X-CH_2-C(O)-O-R_4.

A process for the preparation of the above-mentioned quaternary ammonium compounds has been disclosed in EP-A-21 431. A drawback to the known process described in this document is that it is a comparatively elaborate two-step process, with a secondary amine of the formula R_1-NH-R_2 being converted by addition thereto of an equimolar amount of monochloroacetate ester in the first step, followed by separation of the formed reaction product and addition of a further equivalent amount of monochloroacetate ester in a second step.
The invention now provides a highly simplified, one-step process.
The invention consists in that in a process of the known type mentioned in the opening paragraph

a) a secondary amine of the formula R_1-NH-R_2 is gradually added to and converted with one or more liquid compounds of the formula



at a molar ratio in the range of 1,0:1,0 and 1,0:1,2, in a temperature range from 50 to 110°C, after which
b) the formed solid amine hydrohalide is separated, followed by
c) an aftertreatment, optionally in a solvent, in a temperature range from 40 to 100°C until the conversion is virtually complete, after which, if so desired, further treatments, such as recrystallisation from an organic solvent, are carried out to achieve a special product form.

It was found that when the now proposed process is used, 0,1 to 10 wt.% of the obtained quaternary ester compounds is made up of a monoester quat. Surprisingly, it was found that this presence, preferably in an percentage of 0,2 to 5 wt.%, has a high viscosity reducing effect on diester quat-containing aqueous dispersions.

It should be noted that in WO 93/25648 the preparation of the quaternary diesters mentioned in the opening paragraph also involves the addition of the secondary amine to a solution of chloroacetate esters. However, the amount of secondary amine added is a multiple of that which is added according to the process of the present invention. In consequence, in the known process only the monoester amine is obtained in the first instance; it takes a second step and a second chloroacetate ester for it to be converted to the corresponding diester.

As secondary amine of the formula R1-NH-R_2 may be used symmetrical as well as asymmetrical compounds. Alternatively, mixtures of secondary amines may be employed. Examples of suitable secondary amines include: piperidine, morpholine, methyl ethyl, dipropyl, hydroxyethylmethyl, and diethyl amine. Preference is given in this case to the use of dimethyl amine.
The halogen acetate esters employed may be either chloroacetate esters or bromoacetate esters.

Suitable alcohols for the preparation of the chloro- or bromoacetate esters include branched and linear, saturated and olefinically unsaturated alcohols having 8 to 24 carbon atoms. As examples of the alcohols may be mentioned dodecyl, myristyl, cetyl, oleyl, stearyl, behenyl and/or tallow alcohol. Preference is given in this case to a process in which the secondary amine is dimethyl amine and the halogen acetate esters are tallow chloroacetate esters.

It has been found that the purity of the final product is very much connected with the molar ratio of the secondary amine to the halogen acetate ester. Optimum results were found to be obtained using a process in which the reaction in step a) was carried out at a molar ratio of the secondary amine to the halogen acetate ester(s) in the range of 1,0 : 1,0 to 1,0 : 1,05.

The temperature at which the secondary amine is added is generally in the range of 50° to 110°C, preference being given to addition at a temperature in the range of 60° to 100°C. Adding of the secondary amine commonly takes from 15 minutes to 10 hours, preferably from 30 minutes to 5 hours. Depending on the duration of the addition of the secondary amine, the reaction is continued 5 minutes to 3 hours, preferably 10 minutes to 1,5 hours, at a temperature in the range of 50° to 110°C, preferably in the range of 60° to 100°C.

Finally, the amine hydrohalide is separated from the reaction mixture, e.g., by filtration at a temperature in the range of 90° to 100°C.

The aftertreatment generally is carried out at a temperature in the range of 40° to 100°C, preferably in the range of 50° to 80°C.

The solvent used in the aftertreatment advantageously is ethanol and/or isopropanol. Any further purification is preferably carried out by recrystallisation from a solvent such as methanol, ethanol, propanol, isopropanol, acetone and/or ethyl acetate.

The diester quats obtained in this manner display an outstanding combination of superior softening performance, rapid biodegradability, low algae toxicity and low fish toxicity. Furthermore, they are easy to disperse due to the presence of appropriate amounts of monoester quats whose formation is controlled by the process according to the present invention.

The invention will be further illustrated with reference to the following examples. Of course, the scope of the invention is not restricted to the specific details of the examples.

Example I

In a 1 l glass three-necked flask fitted with a stirrer, a heating jacket, and a dropping funnel 504 g of tallow chloroacetate were heated to 80°C in an atmosphere of nitrogen. 100 ml of dimethyl amine were gradually added over 40 minutes, with care being taken to maintain the reaction temperature of 80°C. Next, the reaction mixture was filtered after heating to 95°C. The filtrate was diluted with 42 g of isopropanol and then subjected to an aftertreatment at 60°C for 3 hours, whereupon, after evaporation of the solvent, dimethyl ditallowester quat was obtained. The product was then dissolved in 3,6 l of acetone and 150 ml of isopropanol. Obtained were 395 g of a white crystalline product composed of 94,1 wt.% of dimethyl ditallowester quat and 2,1 wt.% of trimethyl monotallowester quat.

Example II

The preparation of Example I was repeated up to and including an aftertreatment at 60°C for 3 hours. Finally, the thus obtained product was adjusted with a further 48 g of isopropanol to obtain an 85 per cent solids product containing 81,7 wt.% of dimethyl ditallowester quat and 3,5 wt.% of trimethyl monotallowester quat (in relation to solids).

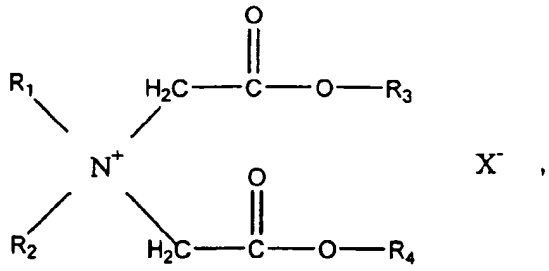
Example III

The following example shows that the presence of a small quantity of mono-ester quat has a surprisingly major effect on the viscosity of a substantially diester quat-containing aqueous dispersion. The diester quat was made up of the dimethyl ditallowester quat of Example I, hereinafter diester quat A. The monoester quat was made up of the corresponding trimethyl monotallowester quat, hereinafter monoester quat M.

aqueous dispersion	I	II	III
diester quat A, wt.%	5,0	5,0	5,0
monoester quat M, wt.%	0	0,2	0,5
viscosity (20°C, mPa.s)	1280	140	50

Claims

1. A process for the preparation of quaternary diesters of the formula:



wherein
X^- represents a halogen atom, notably a chlorine atom or a bromine atom, R_1 and R_2 may be the same or different and have the meaning of an alkyl group having 1 to 3 carbon atoms, a hydroxyethyl group, or be linked together to form an alkylene group having 4 to 6 carbon atoms which may be interrupted by an N atom or O atom, and R_3 and R_4 may be the same or different and have the meaning of an alkyl group or alkenyl group having 8 to 22 carbon atoms, or be linked together to form an alk(en)ylene group having 8 to 22 carbon atoms, characterised in that

a) a secondary amine of the formula R_1-NH-R_2 is gradually added to and converted with one or more liquid compounds of the formula

at a molar ratio in the range of 1,0:1,0 and 1,0:1,2, in a temperature range from 50 to 110°C, after which
b) the formed solid amine hydrohalide is separated, followed by
c) an aftertreatment, optionally in a solvent, in a temperature range from 40 to 100°C until the conversion is virtually complete, after which, if so desired, further treatments, such as recrystallisation from an organic solvent, are carried out to achieve a special product form.

2. A process according to claim 1, characterised in that the reaction in step a) is carried out at a molar ratio of the secondary amine to the halogen acetate ester(s) in the range of 1,0 : 1,0 to 1,0 : 1,05.

3. A process according to claim 1, characterised in that the secondary amine is added at a temperature in the range of 60° to 100°C.

4. A process according to claim 1, characterised in that the amine hydrohalide is separated by filtration at a temperature in the range of 90° to 100°C.

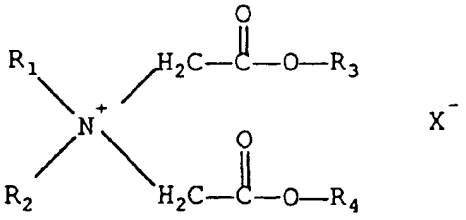
5. A process according to claim 1, characterised in that the aftertreatment according to step c) is carried out at a temperature in the range of 50° to 80°C.

6. A process according to claim 1, characterised in that the solvent employed in the aftertreatment is ethanol and/or isopropanol.

7. A process according to claim 1, characterised in that the solvent employed in the recrystallisation is methanol, ethanol, propanol, isopropanol, acetone and/or ethyl acetate.

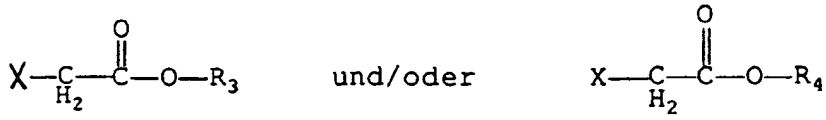
Patentansprüche

1. Verfahren zur Herstellung von quaternären Diestern der Formel:



worin X^- ein Halogenatom, insbesondere ein Chloratom oder ein Bromatom, bedeutet, R_1 und R_2 gleich oder unterschiedlich sein können und die Bedeutung einer Alkylgruppe mit 1 bis 3 Kohlenstoffatomen, einer Hydroxyethylgruppe haben oder miteinander zur Bildung einer Alkylengruppe verbunden sein können, die 4 bis 6 Kohlenstoffe enthält, welche durch ein N-Atom oder ein O-Atom verbunden sein können und wobei R_3 und R_4 gleich oder unterschiedlich sein können und die Bedeutung einer Alkylgruppe oder einer Alkenylgruppe mit 8 bis 22 Kohlenstoffatomen haben oder miteinander zur Bildung einer Alk(en)ylengruppe mit 8 bis 22 Kohlenstoffatomen verbunden sein können, dadurch gekennzeichnet, dass

(a) ein sekundäres Amin der Formel R_1-NH-R_2 langsam zugesetzt und konvertiert wird mit einer oder mehreren flüssigen Verbindung(en) der Formeln



mit einem Molverhältnis im Bereich von 1,0:1,0 bis 1,0:1,2 in einem Temperaturbereich von 50 bis 110°C, worauf
(b) das gebildete feste Aminhydrohalogenid getrennt wird, gefolgt von
(c) einer Nachbehandlung, gewünschtenfalls in einem Lösungsmittel, bei einer Temperatur im Bereich von 40 bis 100°C, bis die Umwandlung praktisch vollständig ist, worauf gewünschtenfalls weitere Behandlungen, wie Umkristallisieren aus einem organischen Lösungsmittel, zum Erzielen einer besonderen Produktform durchgeführt werden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Umsetzung in Schritt (a) mit einem Molverhältnis des sekundären Amins zu Halogenacetatester(n) im Bereich von 1,0:1,0 bis 1,0:1,05 durchgeführt wird.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das sekundäre Amin bei einer Temperatur im Bereich von 60° bis 100°C zugegeben wird.

4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass Aminhydrohalogenid durch Filtration bei einer Temperatur im Bereich von 90° bis 100°C abgetrennt wird.

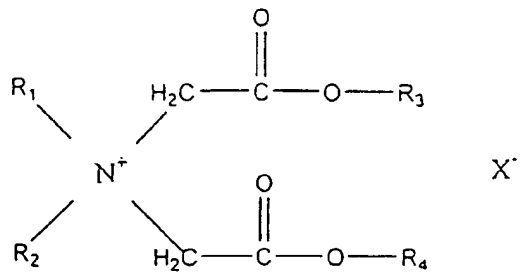
5. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Nachbehandlung gemäss Schritt (c) bei einer Temperatur im Bereich von 50° bis 80°C durchgeführt wird.

6. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das für die Nachbehandlung verwendete Lösungmittel Ethanol und/oder Isopropanol ist.

7. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das für das Umkristallisieren verwendete Lösungsmittel Methanol, Ethanol, Propanol, Isopropanol, Aceton und/oder Ethylacetat ist.

Revendications

1. Procédé de préparation de diesters quaternaires de formule :



dans laquelle :

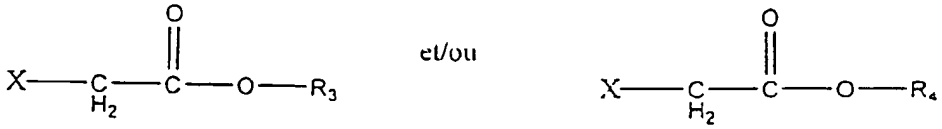
X^- représente un atome d'halogène, notamment un atome de chlore ou un atome de brome,

R_1 et R_2 peuvent être identiques ou différents et représentent un groupe alkyle ayant 1 à 3 atomes de carbone ou un groupe hydroxyéthyle, ou peuvent être reliés ensemble pour former un groupe alkylène ayant 4 à 6 atomes de carbone qui peut être interrompu par un atome d'azote ou un atome d'oxygène, et

R_3 et R_4 peuvent être identiques ou différents et représentent un groupe alkyle ou un groupe alkényle ayant 8 à 22 atomes de carbone, ou peuvent être reliés ensemble pour former un groupe alk(én)ylène ayant 8 à 22 atomes de carbone,

caractérisé en ce que :

a) une amine secondaire de formule R_1-NH-R_2 est ajoutée peu à peu à et convertie par un ou plusieurs composés liquides représentés par les formules :



selon un rapport molaire compris dans la gamme de 1,0:1,0 à 1,0:1,2, dans une gamme de températures allant de 50 à 110°C, après quoi

b) l'halohydrate d'amine solide formé est séparé, puis

c) un post-traitement est effectué, éventuellement dans un solvant, dans une gamme de températures allant de 40 à 100°C jusqu'à ce que la conversion soit pratiquement achevée, après quoi, si cela est désiré, d'autres traitements, comme une recristallisation dans un solvant organique, sont réalisés pour obtenir une forme de produit spéciale.

2. Procédé suivant la revendication 1, caractérisé en ce que la réaction de l'étape (a) est effectuée avec un rapport molaire de l'amine secondaire à l'ester ou aux esters haloacétiques compris dans la gamme de 1,0:1.0 à 1,0:1,05.

3. Procédé suivant la revendication 1, caractérisé en ce que l'amine secondaire est ajoutée à une température comprise dans la gamme de 60° à 100°C.

4. Procédé suivant la revendication 1, caractérisé en ce que l'halohydrate d'amine est séparé par filtration à une température comprise dans la gamme de 90° à 100°C.

5. Procédé suivant la revendication 1, caractérisé en ce que le post-traitement selon l'étape (c) est effectué à une température comprise dans la gamme de 50° à 80°C.

6. Procédé suivant la revendication 1, caractérisé en ce que le solvant employé dans le post-traitement est l'éthanol et/ou l'isopropanol.

7. Procédé suivant la revendication 1, caractérisé en ce que le solvant employé dans la recristallisation est le méthanol, l'éthanol, le propanol, l'isopropanol, l'acétone et/ou l'acétate d'éthyle.